



Flash pyrolysis of model compounds adsorbed on catalyst surface: A method for screening catalysts for cracking of fatty molecules

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ABSTRACT

The aim of this study is to compare the flash pyrolysis of model fatty compounds, that were either pure or adsorbed on different solid catalysts and to use this information for the selection of catalytic materials for renewable fuel production. Myristic acid adsorbed on ZSM-5-type catalysts, methyl oleate adsorbed on γ -alumina, and oleic acid adsorbed on SAPO5-type solids were processed by flash pyrolysis at 650 °C under a helium flow. The main products formed during the decomposition reaction were analyzed on line by gas chromatography/mass spectrometry (GC–MS). In every case, the presence and the nature of the catalysts induced modifications in the type, amount and distribution of the products. Flash pyrolysis of triglycerides and related compounds adsorbed on catalysts may be used as a screening test reaction for the following purposes: (i) to characterize properties of catalysts, and (ii) to confirm the presence of even minute amounts of products, especially primary reaction intermediates.

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1. Introduction

The pyrolysis of fatty compounds has been shown to be useful in the formation of potential fuels and chemicals, and a review on this subject has recently been published [1]. The main conclusions of the recent review are that pyrolysis is able to form highly deoxygenated molecules, such as alkanes, alkenes and aromatics that can be added directly to petroleum fuels.

The pyrolysis of fatty compounds can be slow and fast, with fast pyrolysis leading to lighter compounds. Pyrolysis can also be conducted either with or without a catalyst, and at temperatures ranging from 300 to 800 °C. A higher amount of light products, including gases and compounds with a high degree of deoxygenation, generally results from pyrolysis at higher temperatures or in the presence of catalysts [2–4].

The nature of the fatty compounds also has a significant influence on the composition of the products. Thermal pyrolysis of crude triglycerides and fatty residues at 400–500 °C leads to rather complex liquid products and only moderate yields of deoxygenated compounds [5,6]. Generally, distillation separates those

compounds in fractions compatible with either the gasoline or diesel fraction [2,4–7]. Catalytic pyrolysis also produces a complex liquid mixture, with the surface properties of the catalyst affecting the mixture composition. Acidic catalysts with strong Bronsted sites favor the formation of aromatics and polyaromatics [8], whereas catalysts with moderate or no acidity are able to direct pyrolysis toward the formation of linear saturated and unsaturated hydrocarbons [8,9]. The use of metallic catalysts, such as palladium supported on activated carbon, was shown to produce high amounts of n-C17 alkanes during the thermal decomposition of stearic acid in the presence of n-dodecane at 300 °C under a helium atmosphere [10]. Finally, basic catalysts have also been tested for pyrolysis. These catalysts are generally less efficient for deoxygenation and ketones, and aldehydes are formed. Linear hydrocarbons similar to those obtained when using poorly acidic catalysts are also produced [9,11].

Cracking of fatty model molecules has provided more knowledge of the decomposition mechanisms of triglycerides. Lappi and Alen [3] have decomposed fatty acid sodium salts at temperatures between 450 and 750 °C. Important differences in the product distribution were observed when varying the pyrolysis conditions and the degree of saturation of the fatty acid moiety. Linear saturated and unsaturated hydrocarbons were favored when sodium stearate was pyrolyzed. Lappi and Alen [3] presented strong evidence of decarboxylation and decarbonylation

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followed by dehydration to explain their results. Maher et al. [12] studied the pyrolysis of stearic acid and proposed a mechanism consistent with the deoxygenation reactions cited by Lappi and Alen. Benson et al. [13] built a special set-up where micro amounts of pure fatty acids were injected on a catalyst bed that was connected to on-line gas chromatography with flame ionization detector (GC-FID) and gas chromatography/mass spectrometry (GC-MS) analytical systems. A general mechanism of transformation was proposed. That investigation also showed that the nature of the catalyst has a strong influence on the product distribution. In the great majority of works using catalysts in the decomposition of fatty compounds, the reaction conditions also enabled purely thermal decomposition as well as conversion of the primary products formed.

In the present work, flash pyrolysis of very small amounts of fatty compounds adsorbed on different catalysts has been used as a “pseudo-catalytic test reaction”. This method favors catalytic decomposition over pure thermal decomposition that allows the observation of important differences between catalysts and reacting molecules. The on-line analysis also seems useful for observing primary intermediate compounds during the decomposition of fatty molecules and thus possible reaction steps can be identified.

2. Experimental

2.1. Materials

Fatty acids such as myristic (MA) (Merck) and oleic (OA) (Nuclear) acids, and methyl oleate (MO) (Sigma–Aldrich) were used as model fatty reagents.

2.2. Preparation of the catalysts

- (a) ZSM-5 zeolite: the H form was prepared from $\text{NH}_4\text{ZSM-5}$ (Zeolyst) by thermal treatment at 550°C , under air for 3 h. The Na form was obtained after 3 successive exchanges with an aqueous solution of NaNO_3 (VETEC). At the end of each exchange, the solid phase was separated by filtration and dried at 120°C before being submitted to an additional exchange process. The final exchanged solid was heated at 550°C under air for 3 h.
- (b) γ -Alumina (support of HDT catalysts in extruded form, $S_{\text{BET}} = 210 \text{ m}^2 \text{ g}^{-1}$): the alumina was first manually ground and impregnated with distilled water before drying at 120°C , followed by a heat treatment at 600°C . The impregnation with water was performed to have a true reference support when working with alumina-supported active phases prepared by impregnation via aqueous solutions of precursor salts.
- (c) SAPO-5: SAPO-5 was prepared with the molar composition $0.35\text{SiO}_2 : \text{P}_2\text{O}_5 : \text{Al}_2\text{O}_3 : 1.4(\text{C}_2\text{H}_5)_3\text{N} : 0.072\text{CTMABr} : 4.40\text{hexanol} : 40\text{H}_2\text{O}$, in a two-phase medium, following the previously described methodology [14,15]. The final solid was dried at 110°C and heat treated at 450°C for one hour (heating rate of $10^\circ\text{C min}^{-1}$) under a nitrogen flow of 100 mL min^{-1} . Then, nitrogen was changed for synthetic air and the solid was heated at 550°C (heating rate of $10^\circ\text{C min}^{-1}$) for 5 h.
- (d) NiMo/SAPO-5: This material was prepared by wet impregnation of the SAPO-5 powder with a solution of ammonium heptamolybdate in 21 vol% of H_2O_2 at pH 2 to obtain 5 wt% MoO_3 . The solid was dried at 120°C and calcined in an air flow at 450°C (5°C min^{-1}) for 1 h. The Ni was impregnated using nickel nitrate to obtain 3 wt% NiO. Calcination was carried out using the same conditions as for Mo/SAPO-5.

2.3. Addition of fatty compounds onto the catalysts

Fatty compounds were adsorbed on the powdered form of the solid catalysts. Before adsorption, the catalyst was heat treated at 150 – 200°C to remove most of the adsorbed water. The liquid fatty compounds (oleic acid and methyl oleate) were added to the catalyst by adding micro amounts of organic material, up to 0.1 g per gram of catalyst, under constant manual mixing. Myristic acid, in solid form, was introduced by mechanical co-grinding and followed by a heat treatment at a temperature slightly higher than the fusion temperature, with manual mixing. In the majority of the cases, the preceding process introduced about 10 wt% of organic compound on the solid material, which always maintained its initial powder form. The final materials can be considered as catalysts “impregnated” with fatty organic molecules.

2.4. Characterization of the adsorbed species

To verify the amount of adsorbed organic material on the catalysts and observe its release from the catalysts, thermogravimetric analysis (TG and DTG) were performed for some of the “impregnated” catalysts, using Perkin Elmer STA 6000 equipment, under 20 mL min^{-1} of nitrogen flow. In this case, the system composed by 0.002 g organic fraction “impregnated” in 0.02 g of catalyst was heat treated from room temperature up to 650°C , at a heating rate of $10^\circ\text{C min}^{-1}$. For a comparison experiment, 0.002 g of pure organic compound was also submitted to the TG/DTG experiment, under the same conditions.

2.5. Pyrolysis experiments

Flash pyrolysis was carried out under helium flow in a Pyroprobe 5200 (CDS Analytical) micro-pyrolyzer at 650°C and a estimated heating rate of $1000^\circ\text{C min}^{-1}$ coupled to a Shimadzu QP 2010 Plus GC-MS (Py-GC/MS). The sample was maintained at 650°C for 0.25 min. The GC injector operated in split mode (1:150). A DB-5MS column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) was used for separation of the products. The helium flow rate through the column was 1.0 mL min^{-1} . The temperature of the column oven was ramped from 45 to 240°C at a rate of 4°C min^{-1} and the injector temperature was maintained at 250°C . The GC-MS interface temperature was 290°C , the ion source temperature was 250°C and m/z was analyzed in the range of 45–400. Approximately 0.1 mg of fatty compound/catalyst was used. The helium flow rate through the sample was 150 mL min^{-1} . The peaks from GC-MS were identified by comparison of their mass spectrometry fragmentation patterns with data from the NIST library. Identification of the majority of products was based on a probability match equal or higher than 90%. The identification of products was also supported by literature data [1–3,5].

3. Results and discussion

3.1. Pyrolysis of myristic acid adsorbed on ZSM-5 type material

Fig. 1 shows thermogravimetric curves obtained when heating pure myristic acid (MA) and MA adsorbed on NaZSM-5 (MA/NaZSM-5) and HZSM-5 (MA/HZSM-5) catalysts. For pure myristic acid, a single weight loss with a maximum rate at 230°C was observed. Under flash pyrolysis conditions, the experiment with pure myristic acid did not allow the detection of significant amount of low molecular weight products due to myristic acid decomposition. Only untransformed myristic acid was observed by GC-MS (Fig. 2). This suggests that pure myristic acid in the TG experiment leaves the sample holder without an important chemical transformation. The TG/DTG thermogram of myristic acid

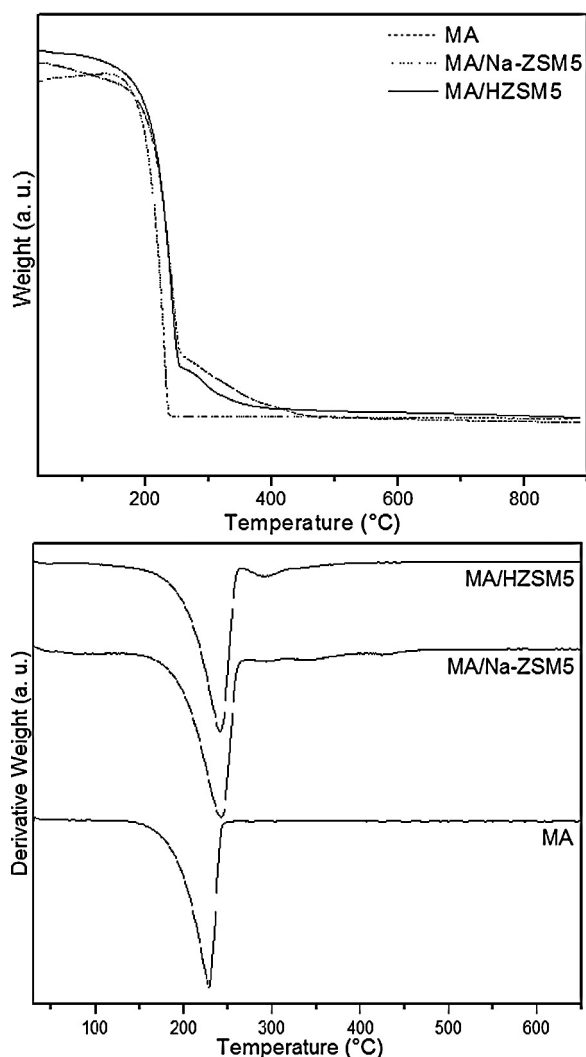


Fig. 1. TG/DTG curves up to 650 °C (10 °C min⁻¹) under N₂ flow of myristic acid (MA) either pure or adsorbed on both NaZSM-5 and HZSM-5 catalysts. The TG results were obtained with 0.002 g of MA in each case.

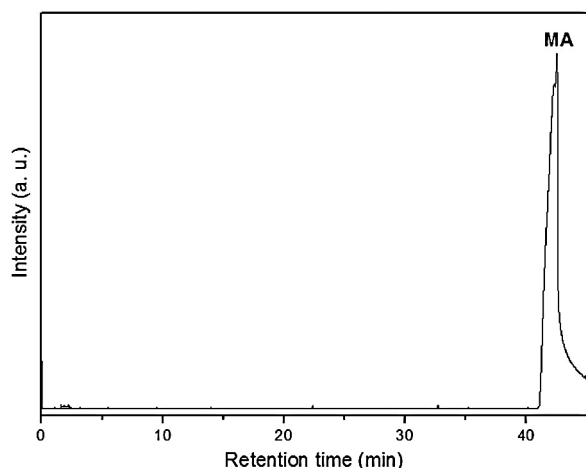


Fig. 2. Total ion chromatogram from flash pyrolysis at 650 °C of pure myristic acid.

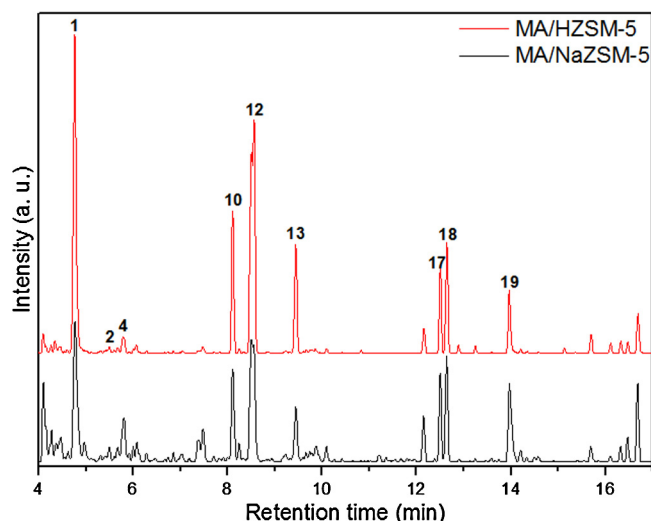


Fig. 3. Total ion chromatograms showing products from flash pyrolysis at 650 °C of myristic acid (MA) adsorbed on NaZSM-5 (black line) and HZSM-5 (red line), retention times between 4 and 17 min. Peak numbers refer to compounds identified in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

adsorbed on ZSM-5 materials showed a maximum weight loss shifted to 245 °C. The shift of this main peak is partially attributed to heat transfer limitations of the adsorbed myristic acid on catalyst (sample weight of 0.022 g) in comparison with the pure myristic acid (0.002 g). However the shift of the main peak in the DTG of MA/catalyst also demonstrates the interaction of the fatty acid with solid surface. This main weight loss of myristic acid adsorbed on catalysts was followed at higher temperatures by smaller weight loss events, a contrasting result for both systems. These observations suggest that myristic acid adsorbed on ZSM-5 materials decomposed differently than pure myristic acid.

In the pyrogram of pure myristic acid (Fig. 2) just one peak appears after 40 min, which reveals that under the present experimental conditions the conversion of pure myristic acid is negligible. Fig. 3 shows a portion of the pyrograms obtained after the flash pyrolysis of myristic acid adsorbed on Na- and H-ZSM-5 solids at 650 °C respectively. Table 1 gives the main products identified in both pyrograms from Fig. 3. Although the two pyrograms in Fig. 3 present many similarities, some differences appear and confirm that myristic acid is not pyrolyzed exactly in the same way after adsorption on both catalysts, in agreement with TG/DTG results in Fig. 1.

Table 2 displays the semi-quantitative results obtained from the whole pyrograms obtained for both MA/NaZSM-5 and MA/HZSM-5 systems. Table 2 indicates that the conversion of MA is far from complete and that HZSM-5 is a more efficient support than NaZSM-5 for decomposing adsorbed myristic acid. Additionally, the amount of unidentified and identified oxygenated compounds, other than myristic acid, is similar in both cases, although the amount of hydrocarbons produced by the decomposition is much higher using the MA/HZSM-5 system than MA/NaZSM-5. Table 2 also provides the distribution between the main groups of products (limited to the interval C3–C13) obtained from the decomposition of MA adsorbed on both catalysts. The pyrolysis of MA on NaZSM-5 produced mainly monoolefins, monoaromatics and polyolefins whereas the pyrolysis on HZSM-5 produced mainly monoolefins, monoaromatics, polyaromatics and saturated hydrocarbons. The higher amount of aromatics and saturated products obtained in this latter case is attributed to the acidic character existing in HZSM-5 favoring hydrogen transfer reactions, according to results obtained

Table 1

Retention time (t_R), % area and proposed identification of the major products detected, from 4.7 to 17.0 min, during the flash pyrolysis of myristic acid (MA) adsorbed on NaZSM-5 and HZSM-5 at 650 °C.

	t_R (min)	Compound	Formula	MA/NaZSM-5	MA/HZSM-5
1	4.792	Toluene	C7H8	2.04	4.58
2	5.505	1-Octene	C8H16	0.13	0.09
3	5.695	3-methyl-4-methylene-Hexane	C8H16	0.15	
4	5.821	Hexanal	C6H12O	0.82	
5	5.837	1-Octanol	C8H18O		0.09
6	6.100	Ethylidene cyclohexane	C8H14	0.12	
7	6.109	4-methyl-1,3-Heptadiene	C8H14		0.07
8	7.417	2,5,5-trimethyl-Cyclopentadiene	C8H12	0.15	
9	7.503	1,2-dimethyl-1-Cyclohexadiene	C8H12	0.25	
10	8.133	Ethylbenzene	C8H10	0.70	1.25
11	8.264	3-ethylidene-1-methyl-Cyclopentene	C8H12	0.13	
12	8.571	m + p-Xylene	C8H10	1.83	3.85
13	9.474	o-Xylene	C8H10	0.54	0.81
14	9.940	Heptanal	C7H14O	0.27	
15	10.107	(E)-2-Nonene	C9H18	0.09	
16	12.171	propyl Benzene	C9H12	0.27	0.12
17	12.524	1-ethyl-2-methyl-Benzene	C9H12	0.65	0.63
18	12.657	1-ethyl-3-methyl-Benzene	C9H12	0.70	0.71
19	13.991	1,2,3-trimethyl-Benzene	C9H12	0.69	0.53
20	14.482	Octanal	C8H16O	0.15	
21	15.711	2-propenyl-Benzene	C9H10	0.11	
22	15.721	1-ethenyl-2-methyl-Benzene	C9H10		0.11
23	16.336	1,4-diethyl-Benzene	C10H14	0.10	
24	16.483	1-methyl-3-propyl-Benzene	C10H14	0.16	
25	16.697	1,2-diethyl-Benzene	C10H14	0.46	0.19

in classical catalytic reactors [16–18]. The increased formation of polyaromatics (indenes and naphthalenes) during the pyrolysis of MA/HZSM-5 compared to MA/NaZSM-5 is consistent with the higher acidity of HZSM-5 compared to NaZSM-5.

The main products obtained in both cases (see partial identification in Table 1) are deoxygenated compounds. This implies that during the pyrolysis of myristic acid, the molecule is essentially deoxygenated via decarboxylation and/or decarbonylation, and that the primary products, mainly those with unsaturated double C=C bonds are further transformed into cracked products, as recently confirmed [19]. In the products identified in Fig. 3, some saturated aldehydes (C6–C8) were formed during the pyrolysis of MA/Na-ZSM-5, but were not detected in the pyrolysis of MA/H-ZSM-5. In the complete pyrogram, tetradecanal with retention time around 33 min was identified in both MA/Na-ZSM-5 (1.66% area) and MA/H-ZSM-5 (0.66% area). Therefore, the formation of aldehydes is favored in the presence of Na. A sodium salt of myristic acid may be formed during the adsorption of myristic acid on the samples, parallel to the adsorption of pure myristic acid. The chemical adsorption of carboxylic acids with the formation of carboxylate species on different solids has been described in the literature [20]. The fact that short chain aldehydes are observed, although in small amount, suggests that in parallel to myristic acid deoxygenation, the molecule can be cracked inside the saturated carbon chain, leading to short-chain carboxylic acids. These intermediate carboxylic acids can be the precursors for short-chain aldehydes and short chain unsaturated hydrocarbons, an important fraction of the detected products. Several other investigations have reported the formation of short-chain carboxylic acids during the pyrolysis of triglycerides and related compounds [1,2,21,22].

Table 2

Semi quantitative distribution (% area in GC–MS data) of product families obtained during flash pyrolysis at 650 °C of myristic acid adsorbed on NaZSM-5 and HZSM-5 catalysts: MA = untransformed myristic acid, NI + Ox = unidentified + oxygenated products, HC = deoxygenated products, Mono-O = monounsaturated hydrocarbons, Poly-O = polyunsaturated hydrocarbons, Mono-A = monoaromatics, Poly-A = indenes and naphthalenes. The semi quantitative estimation of these products is limited to compounds with carbon number between 3 and 13.

Catalyst	MA	NI + Ox	Total HC	Sat	Mono-O	Poly-O	Mono-A	Poly-A
MA/NaZSM-5	69.2	14.5	16.3	0.2	9.4	1.7	4.9	0.1
MA/HZSM-5	54.8	12.3	32.9	1.4	15.4	0.8	13.5	1.8

Therefore, the present experiments clearly show that adsorbed myristic acid did not decompose through identical reaction pathways on purely acidic HZSM-5 or acido-basic NaZSM-5 catalyst. In the case of HZSM-5, the presence of 1-octanol did not seem characteristic of an acid catalyst, as alcohols are readily decomposed to olefins at elevated temperatures on acidic catalysts [23]. At most, the present observation indicates that aldehydes are reduced to alcohols on acidic catalysts most likely through the hydrogen transfer reaction, and that these alcohols can be further dehydrated to olefins when the experimental conditions are optimized. Another and more likely hypothesis also exists: in the transfer line joining the pyrolysis cell to the analytical system (maintained at temperature close to 250 °C), recombination occurs between olefins and traces of water vapor to form alcohols.

This first example illustrates that the flash pyrolysis of myristic acid adsorbed on ZSM-5-type materials is very effective at decomposing myristic acid into deoxygenated low molecular weight compounds, and particularly into aromatic compounds that contain fewer C atoms than the reacting molecule. This result agrees with the general trends observed when cracking fatty compounds in the presence of zeolite catalysts in more traditional reaction devices [8,24,25]. The presence of Na in ZSM-5 may modify some steps of the decomposition pathways, as it makes it possible to form a significant amount of aldehydes in the products.

3.2. Pyrolysis of methyl oleate pure (MO) or adsorbed on γ -alumina (MO/ γ -alumina)

Fig. 4 shows a fraction from the pyrograms (retention times between 35.5 and 53.9 min) obtained during the flash pyrolysis at 650 °C of pure methyl oleate (MO) and Mo/ γ -alumina. A

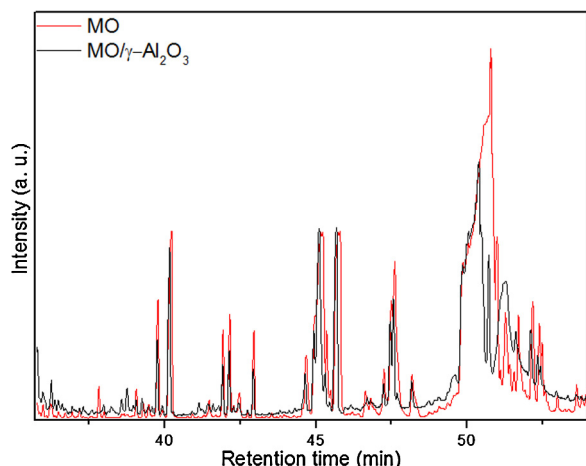


Fig. 4. Total ion chromatograms showing products from flash pyrolysis at 650 °C of methyl oleate (MO) either pure (red line) or adsorbed on γ -alumina (black line), retention times between 35.5 and 54.0 min. The main peaks around retention times 40, 42–43, 45–46, 48 and 50–51 min are attributed to methyl esters with respectively 15, 16, 17, 18 and 19 carbons in their structure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

complete analysis of the main products appearing in the pyrograms, shown in Fig. 4, is not very simple because the peak separation is not well defined and the NIST library offers a variety of molecules for each pyrogram peak. Further, the actual NIST library may not offer all of the possible isomers for compounds such as unsaturated methyl esters with a carbon number in the range C15–C19. For the present analysis, the main peaks around retention times 40, 42–43, 45–46, 47–48 and 50–53 min are all attributed to methyl esters with respectively 15, 16, 17, 18 and 19 carbons in their structure. Further, the % area of the C19 methyl esters is smaller in the pyrolysis of MO/ γ -alumina than in the pyrolysis of pure MO. In both cases, MO decomposes qualitatively in a similar way. On the other hand, the pyrolysis in presence of γ -alumina promotes a higher extent of MO decomposition. The presence of methyl esters with smaller chain lengths than methyl oleate is an indication that, as seen before with myristic acid, methyl oleate can be cracked inside the carbon chain of the molecule and not only near the carboxylic acid group.

Methyl esters in the range of C15–C19 are the main compounds observed after the pyrolysis of both MO/ γ -alumina and pure MO: only minor differences among them are observed. This suggests that γ -alumina has a limited effect on the formation of high molecular weight products most likely because not all of the methyl oleate is strongly adsorbed on γ -alumina.

However the product distribution in the range of C6–C12 is affected by the γ -alumina catalyst, compared to the products from the thermal degradation of pure MO. These products are shown in Fig. 5 and Table 3 which provides a semi-quantitative analysis of the main peaks in Fig. 5.

Fig. 5 shows pyrograms with retention times between 4.4 and 22.6 min. Although the analyzed peaks represent a rather small fraction of the whole pyrogram, some points are indicative: (i) the

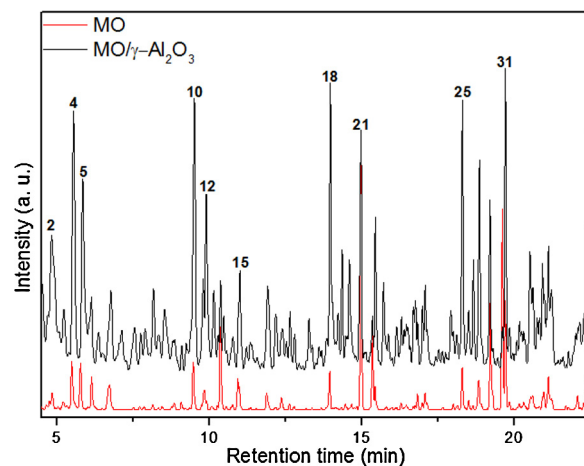


Fig. 5. Total ion chromatograms showing products from flash pyrolysis at 650 °C of methyl oleate (MO) either pure (red line) or adsorbed on γ -alumina (black line), retention times between 4.4 and 22.6 min. Peak numbers refer to compounds identified in Table 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

pyrolysis of pure MO produced mainly C6–C9 methyl esters; (ii) the presence of γ -alumina for the catalyst-assisted pyrolysis increases the deoxygenation of short chain esters producing mainly hydrocarbons (Table 3).

Table 4 presents the main products identified in the pyrograms in Fig. 5, including their retention time and their relative % area.

The pyrograms in Fig. 5 clearly illustrate that the number and the quantity of products obtained from catalytic pyrolysis of MO/ γ -alumina are higher than those obtained in the thermal pyrolysis of pure MO.

Table 3 summarizes semi quantitative results from the product compounds of Table 4. The results in Table 3, which show area percentage from the pyrolysis of MO/ γ -alumina (50 peaks) and of pure MO (30 peaks) confirm that the presence of the catalyst strongly favors the decomposition of MO. Under these reaction conditions, the light compounds obtained in the presence of γ -alumina are mainly the result of catalytic reaction between specific sites of the γ -alumina and the adsorbed fatty moieties and are therefore different from pyrolysis of pure MO. In addition to better conversion, improved deoxygenation is obtained, as well as a better cracking. When looking at the fine composition of the hydrocarbon fraction, alkanes (0.1%), monounsaturated (0.5%) and polyunsaturated (0.5%) compounds are obtained when pyrolyzing pure MO, as shown in Table 4. For the pyrolysis of MO/ γ -alumina, the hydrocarbon distribution is different, with more alkanes (1.4%), monounsaturated (6.0%), polyunsaturated (3.4%) and aromatic compounds (1.8%) observed. The formation of aromatics is therefore associated to a property of the γ -alumina and most likely due to the presence of some acidic sites, as alumina is generally considered to possess Lewis acidic character [26]. Within polyunsaturated compounds, linear diolefins and linear alkynes were observed in the pyrolysis of pure MO, whereas small amounts of trienes and unsaturated cyclic compounds were identified after the pyrolysis of MO/ γ -alumina. These compounds can be considered as potential intermediates between mono- and di-olefins formed during pyrolysis of pure MO, and aromatics, formed during catalytic pyrolysis. Finally, whereas 1-alkenes are obtained from the pyrolysis of pure MO, numerous other alkene isomers, as well as some cyclic olefins, were obtained after the pyrolysis of MO/ γ -alumina. These compounds must also result from the acidic sites of the γ -alumina during pyrolysis.

The number of methyl esters of carboxylic acids observed in both pyrolysis of pure MO and in the presence of catalyst implies

Table 3

Semi-quantitative distribution (% area in GC–MS data) of the product families obtained in the chromatogram portion of Fig. 5: All peaks = % area of all the peaks in the fragment versus the area of all peaks in the whole chromatogram, NI = % area of unidentified peaks, oxygenated = % area of all oxygenated compounds, HC = % area of hydrocarbons, and esters = % area of methyl esters.

	All peaks	NI	Oxygenated	HC	Esters
Pure MO	2.8	0.1	1.6	1.1	1.5
MO/ γ -alumina	14.9	1.1	0.9	12.8	0.7

Table 4

Retention time (t_R), % area and proposed identification of the major products detected, from 4.4 to 22.6 min during the flash pyrolysis at 650 °C of pure methyl oleate (MO) and MO adsorbed on γ -alumina. NI = unidentified compounds.

	t_R (min)	Compound	Formula	MO	MO/ γ -alumina
1	4.523	ethylidene-Cyclopentane	C7H12		0.37
2	4.829	Toluene	C7H8		0.71
3	5.229	3-ethenyl-Cyclopentene	C7H10		0.23
4	5.551	1-Octene	C8H16	0.11	0.75
5	5.852	n-Octane	C8H18	0.10	0.63
6	6.136	(E)-2-Octene	C8H16		0.29
7	6.139	methyl ester 4-Pentenoic acid	C6H10O2	0.07	
8	6.775	Octadiene	C8H14	0.09	0.32
9	8.165	m + p-Xylene	C8H10		0.24
10	8.528	1,9-Decadiene	C10H14		0.29
11	9.508	1-Nonene	C9H18	0.10	0.74
12	9.797	Cyclooctene	C8H14		0.23
13	9.896	n-Nonane	C9H20		0.42
14	10.144	(E)-2-Nonene	C9H18		0.22
15	10.365	5-Hexenoic acid methyl ester	C7H12O2	0.16	0.15
16	10.926	Hexanoic acid methyl ester	C7H14O2	0.05	
17	11.000	1,3-Nonadiene	C9H16		0.28
18	11.909	1-butyl-Cyclopentene	C9H16		0.29
19	12.175	propyl-Benzene	C9H12		0.16
20	13.962	1-Decene	C10H20	0.06	0.61
21	14.350	n-Decane	C10H22		0.20
22	14.589	(E)-2-Decene	C10H20		0.29
23	14.967	6-Heptenoic acid methyl ester	C8H14O2	0.49	0.45
24	15.347	Heptanoic acid methyl ester	C8H16O2	0.13	
25	15.440	5-Decyne	C10H18		0.28
26	15.708	1-Propenyl-Benzene	C9H10		0.22
27	17.072	1H-Indene	C9H16		0.23
28	18.282	(Z)-2-Undecene	C11H22	0.08	
29	18.291	1-Undecene	C11H22		0.49
30	18.492	(E)-5-Undecene	C11H22		0.17
31	18.652	Undecane	C11H24		0.20
32	18.826	Nonanal	C9H18O	0.05	
33	18.851	(Z)-2-Undecene	C11H22		0.42
34	19.193	(E)-4-Undecene	C11H22		0.33
35	19.208	3-Octenoic acid methyl ester	C9H16O2	0.22	
36	19.600	Octanoic acid methyl ester	C9H18O2	0.35	
37	19.698	Z-1,6-Undecadiene	C11H20	0.18	
38	19.701	5-Undecyne	C11H20		0.50
39	20.505	NI			0.28
40	20.915	NI			0.17
41	20.965	5-Undecen-3-yne	C11H18	0.05	
42	21.110	trans-trans-2,9-Undecadiene	C11H20	0.07	0.25
43	21.209	2-Undecyne	C11H20		0.23
44	22.355	1-Dodecene	C12H24	0.05	0.53

that one of the first steps in the MO fatty compound decomposition is most likely an internal migration of the double bond, followed by cracking in both β positions of this double bond. After cracked, the methyl esters are deoxygenated via decarboxylation and decarbonylation reactions producing unsaturated hydrocarbons [1].

In this second example, flash pyrolysis at 650 °C of MO either pure or adsorbed on γ -alumina indicates that (i) the main products formed with and without catalysts are methyl esters of carboxylic acids and their isomers; (ii) the presence of γ -alumina facilitates further decomposition of the intermediate products, and particularly the deoxygenation reaction; (iii) mono-, di- and tri-unsaturated hydrocarbons as well as aromatics are formed when MO is adsorbed on γ -alumina; (iv) the shift in the position of the C=C bond of methyl oleate is an important step before or during cracking reactions.

3.3. Comparison of the products obtained from pyrolysis of oleic acid, after adsorption on SAPO-5 and NiMo/SAPO-5

Fig. 6 presents the pyrograms of the products, with retention times between 4.5 and 24 min, obtained after the flash pyrolysis at 650 °C of oleic acid adsorbed on SAPO-5 (black line) and on NiMo/SAPO-5 (red line), whereas Table 5 shows the main products identified in Fig. 6 through GC–MS analysis. The great majority of

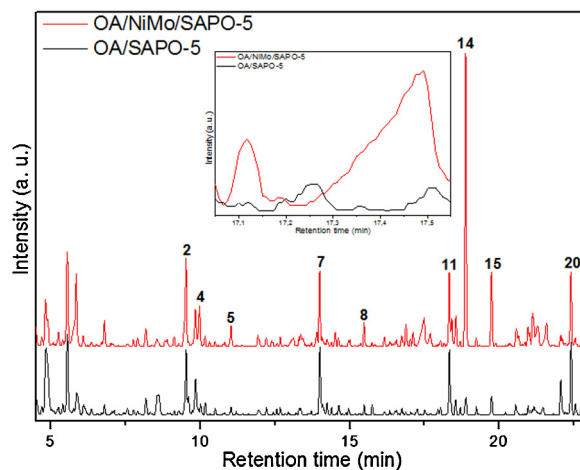


Fig. 6. Total ion chromatograms showing products from flash pyrolysis at 650 °C of oleic acid (OA) adsorbed on both SAPO-5 (black line) and NiMo/SAPO-5 (red line), retention times between 4.4 and 24 min. The inserted window presents a zoom of a triangular peak around retention time 17.5 min, attributed to 3-heptenoic acid, in the case of the pyrolysis of OA adsorbed on NiMo/SAPO-5. Peak numbers refer to compounds identified in Table 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 5
Retention time (t_R), % area and proposed identification of the peaks present in the chromatogram in Fig. 6, during the flash pyrolysis at 650 °C of oleic acid (OA) adsorbed on both NiMo/SAPO-5 and SAPO-5. NI = unidentified compounds.

	t_R (min)	Compound	Formula	NiMo/SAPO-5	SAPO-5
1	8.180	1,5-Octadiyne	C8H10	0.11	
2	8.599	m + p-Xylene	C8H10		0.21
3	9.518	1-Nonene	C9H18	0.54	0.23
4	9.836	Cyclooctene	C8H14	0.17	
5	9.838	1,7-Octadiene	C8H14		0.16
6	9.968	Heptanal	C7H14O	0.19	
7	11.029	1,8-Nonadiene	C9H16	0.11	
8	13.120	5-Hexenoic acid	C6H10O2	0.08	
9	13.991	1-Decene	C10H20	0.32	0.25
10	15.477	5-Decyne	C10H18	0.12	
11	16.875	2,3,6-trimethyl-Heptadiene	C10H18	0.11	
12	17.489	3-Heptenoic acid	C7H12O2	0.33	
13	18.329	1-Undecene	C11H22	0.37	0.29
14	18.416	2-ethyl-4-Pental	C7H12O	0.13	
15	18.534	(Z)-2-methyl-3-Decene	C11H22		0.06
16	18.548	(Z)-4-Undecene	C11H22	0.15	
17	18.878	Nonanal	C9H18O	1.60	
18	18.891	(E)-2-Undecene	C11H22		0.09
19	19.742	1,4-Undecadiene	C11H20	0.37	
20	19.745	NI			0.07
21	20.962	NI		0.10	
22	21.115	2-Nonenal	C9H16O	0.20	
23	21.285	Cyclohexanepropanol	C9H18O	0.12	
24	21.588	Octanoic acid	C8H16O2	0.18	
25	22.061	1-methylene-1H-Indene	C10H8		0.16
26	22.400	1-Dodecene	C12H24	0.35	0.28

the main products, in particular 1-alkenes, exist after pyrolysis with either catalyst. Clearly, the number of products detected is more important in the case of NiMo/SAPO-5 than in the case of SAPO-5, and the peak area is often higher in the case of NiMo/SAPO-5. These two observations suggest that NiMo/SAPO-5 is more active than SAPO-5 and is responsible for a more complex reaction scheme during the pyrolysis of oleic acid.

In the case of pyrolysis of oleic acid adsorbed on NiMo/SAPO-5, carboxylic acid products are detected at retention times close to 13.1, 17.5 and 21.6 min and were identified, respectively, as 5-hexenoic acid, 3-heptenoic acid (see window in Fig. 6) and octanoic acid. These compounds are practically not found in the flash pyrolysis of oleic acid adsorbed on SAPO-5. This result indicates that the decarboxylation and decarbonylation of oleic acid are not always the first reaction step in the degradation of oleic acid, as is often suggested in the literature [1] for the thermal conversion of fatty acids, but that cracking inside the carbon chain, most likely close to the C=C double bond, also occurs [19]. The formation of small carboxylic acid products has been observed before [2] and was recently analyzed [21] during the decomposition of fatty acids. Such a situation is observed for the unsaturated lateral chain of a fatty acid and was also noted during the pyrolysis of myristic acid described above (Section 3.1). The fact that saturated and unsaturated C6, C7, and C8 carboxylic acids are present as shown Fig. 6 suggests that oleic acid cracking can occur on both sides of the C=C double bond; -such a C=C double bond has been able to migrate to some extent along the carbon chain-, before the cracking occurs, as has been advocated in the pyrolysis of methyl oleate, also described above (Section 3.2).

At retention times close to 5.84, 9.97, 18.88 and 21.11 min, peaks are attributed to hexanal, heptanal, nonanal and 2-nonenal, respectively for the system OA/NiMo/SAPO-5. The formation of aldehydes is most likely due to the presence of a specific oleic acid decomposition pathway. After cracking inside the lateral carbon chain, simple mono-deoxygenation of acidic moieties occurs. The formation of sodium carboxylate was suggested in the case of myristic acid adsorbed on NaZSM5 to explain the important formation of C6, C7 and C8 aldehydes. On the other hand, it is possible that with OA/NiMo/SAPO-5, the reduced sites of the NiMo species

are sites for a single oxygen removal from the carboxylic group. Then, low molecular weight fatty acid can be reduced to aldehyde. Literature data indicates that NiO can be partially reduced to metallic nickel in the presence of hydrocarbons, at temperatures close to 400 °C [27,28]. The presence of polyunsaturated compounds such as 1,3-octadiene, 1,8-nonadiene, 2,3,5-trimethylheptadiene, 1,4-undecadiene, 1,5-octadiyne and 5-decyne for the system OA/NiMo/SAPO-5 also seems in agreement with the dehydrogenation abilities of NiMo/SAPO5, which are possibly linked to the presence of partially reduced metal species as suggested above.

In Fig. 5 at retention times between 8 and 9 min, a more intense peak appears after the pyrolysis of oleic acid adsorbed on SAPO-5 than when oleic acid is adsorbed on NiMo/SAPO-5. This intense peak is due to the formation (m + p)-xylenes, and is often linked to catalyst acidity [24]. Another aromatic compound observed only on SAPO-5 at retention time 22.06 min is identified as methylene-1H-indene, which is attributed to the stronger acidic sites of SAPO-5 compared with SAPO-5 modified by Mo [15].

In this third example, the pyrolysis of oleic acid adsorbed on SAPO-5-type materials showed a rather high selectivity toward terminal olefins, but a much smaller selectivity toward aromatic compounds than a strongly acidic catalyst. Such a property reported with other metal catalysts [29] could be interesting for the preparation of fuel additives and/or specific organic chemicals with fewer amounts of aromatic compounds.

3.4. Final comments

The direct comparison of the present results with other data in the literature is difficult because other researchers have not investigated the pyrolysis of fatty compounds adsorbed on catalysts. However, some points can be extracted from the study of Lappi and Allen [3], in which the flash pyrolysis of fatty acid sodium salts in a temperature range 500–750 °C was implemented. First, Lappi and Allen [3] stated that their micro pyrolysis set-up, which was similar to the one employed in this work, has some limitations. In particular working with micro-amounts of reactants does not always provide perfect quantitative data, and related to their pyrolysis instrument, some heavy compounds may condense in the transfer line between

the pyrolysis area and the analysis area and eventually desorb with products from another pyrolysis. This difficulty was also noted in the present experiments, which were always performed after an extensive cleaning procedure to limit detecting unexpected products. Second, in the experiments of Lappi and Alen [3] performed at 650 °C, as in the present study, the amount of unidentified products was often in the range of 20–25%. The present results also suffer from this problem: the separation of light products was not very precise, and for the heavy products, the NIST library did not always offer a choice of compounds coherent with the pyrolysis of fatty compounds. However, the present results, in agreement with Lappi and Alen [3], seemed sufficient to show clear trends between different experiments.

After the pyrolysis of sodium oleate at 650 °C, Lappi and Alen [3] listed the components of various classes of products: alkenes, ring-containing alkenes, alkanes, ring-containing alkanes, dienes, aromatics and oxygen-containing compounds. In the present study, during the flash pyrolysis of methyl oleate either pure or adsorbed on γ -alumina, all of these classes of products were also observed (see Table 4), suggesting that the main reaction pathways in the pyrolysis of Lappi and Alen [3] also exist in the present study. However, as the conversion obtained in the present study is lower than the practically complete conversion observed in the case of pyrolysis of sodium salts of fatty acids, detecting intermediary products is possible. This idea explains why methyl esters of carboxylic acids, alkynes and aldehydes were identified in the present study. Alkynes, aldehydes and alcohols (as well as carboxylic acids) were observed by Fortes and Baugh [22] in their study of pyrolysis of vegetable oils from Macauba fruit. In their experiments, the vegetable oil was dispensed as a thin film on the filament of their pyrolyzer device, a situation not very different from the experimental procedure used in the present study, where instead of deposited onto the filament, the fatty compounds were adsorbed onto the surface of the catalysts.

Boocock et al. [30] obtained liquid yields between 41% (coconut oil) and 73% (triolein) in their study of pyrolysis (up to 450 °C) of triglycerides over activated alumina. The main products detected after the pyrolysis of triolein and trilaurin were 1-alkenes, n-alkanes and some n-alkene isomers. With triolein and trilaurin pyrolysis, products with hydrocarbon chains varying between C6–C7 and C9–C11 presented the highest content among all other hydrocarbons. Small amounts of compounds with carbonyl groups were also present and were identified as carboxylic acids. Importantly, Boocock et al. [30] did not observe aromatic compounds in their liquid pyrolyzate, whereas in the present study various aromatics were observed. Two points may explain such differences: (i) the temperature of pyrolysis is much higher in the present study, favoring further transformation of linear unsaturated compounds; (ii) the activated alumina used in [30] may have a much lower acidity than the γ -alumina used in the present work, as activated alumina surfaces often have high sodium content. In a pyrolytic study of decarboxylation and cracking of stearic acid, Maher et al. [12] showed that under their experimental conditions untransformed stearic acid was often detected together with light products. The presence of unreacted reagent was always observed in the present experiments. Therefore, these earlier results may be compared with the present ones. Maher et al. [12] performed the pyrolysis of stearic acid between 350 and 450 °C, in closed reactors, and at autogenous pressure. Increasing the reaction time and temperature led to the formation of a higher number of lighter products. Among the main products, n-alkanes and alkenes were obtained. However saturated and unsaturated fatty carboxylic compounds were also identified. The major product observed was generally n-heptadecane, resulting from a simple decarboxylation of stearic acid. At pyrolysis temperatures of 450 and 500 °C, aromatic compounds were also obtained, including toluene, xylenes,

indenes, naphthalenes and heavier polyaromatic species. The aromatic formation during cracking and pyrolysis of triglycerides and related compounds has been observed in many studies such as the previously mentioned review [1]. In the pyrolysis of palm oil on HZSM-5, Twaiq et al. [31] and Ooi et al. [32] obtained yields as high as 40% for aromatics, essentially benzene, toluene and xylenes.

The results of the present study are generally in qualitative agreement with the preceding ones, and show by direct comparison that the pyrolysis of pure methyl oleate is distinct from the catalytic pyrolysis of this reagent. The present results also show that the presence of sodium in ZSM-5 zeolite modifies the distribution and nature of the products during the catalytic pyrolysis of myristic acid, a fatty acid that did not show decomposition when submitted to pyrolysis without catalyst under the same experimental conditions. Finally, this work showed that SAPO-5-type catalysts favored the production of 1-alkenes.

Therefore, the method proposed in this work by performing the flash pyrolysis of small amounts of reactants adsorbed on solid catalysts may be considered a rapid screening method that reveals the catalytic properties and possible reaction pathways.

4. Conclusions

The three examples reported in the present study show that these experimental conditions for the flash pyrolysis of fatty materials adsorbed on catalysts are an useful way to reveal the catalytic properties of the catalyst and can help in the selection of catalysts before long-term catalytic experiments are performed. In fact, the main products obtained in traditional catalytic reactions are generally observed during the flash pyrolysis of adsorbed species, although the quantitative data are not directly comparable. One of the further benefits of the flash pyrolysis of fatty compounds adsorbed on solid catalysts is that some insights into the initial reaction mechanisms are also possible. In particular, the flash pyrolysis of fatty compounds adsorbed on catalytic materials seems to be very useful to show the production of polyunsaturated hydrocarbons, aromatics, and intermediate oxygenated compounds such as alcohols, aldehydes, small-chain carboxylic acids and esters of carboxylic acids in the particular case of pyrolysis of methyl oleate. An analysis of the products formed may help better understand the complex mechanism of the pathways involved in the thermal decomposition of triglycerides and related compounds. In particular, the present experimental approach has clearly revealed the possibility of cracking inside the carbon chain of fatty compounds as an initial step in the degradation of triglycerides and related compounds, together with the well-established decarboxylation and decarbonylation reactions.

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